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Theoretical studies of the free energies of electron transfer and electron transfer kinetics in nanostructure supramolecular complexes of *cis*-unsaturated thiocrown ethers and Ce and Gd endohedral metallofullerenes $[X-UT-Y][M@C_{82}]$ ($M = Ce, Gd$)



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Abstract Unsaturated thiocrown ethers (described as $[X-UT-Y]$, where X and Y indicate the numbers of carbon and sulfur atoms, respectively) with *cis*-geometry are a group of crown ethers that, in light of the size of their cavities and their conformational restriction compared to a corresponding saturated system (**1–9**), demonstrate interesting properties for physicochemical studies. Formation of endohedral metallofullerenes is thought to involve the transfer of electrons from the encapsulated metal atom(s) to the surrounding fullerene cage. Two of these molecules are the $Ce@C_{82}$ (**10**) and $Gd@C_{82}$ (**11**). The supramolecular complexes of **1–9** with $Ce@C_{82}$ (**10**) and $Gd@C_{82}$ (**11**) have been shown to possess a host–guest interaction for electron transfer processes, and these behaviors have previously been reported. The relationship between an index (which was introduced as the ratio of summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s)) and oxidation potential ($^{ox}E_1$) of **1–9**, as well as the free energies of electron transfer (ΔG_{et} , by the Rehm–Weller equation) between **1–9** and **10** and **11** as $[X-UT-Y][Ce@C_{82}]$ (**12**) and $[X-UT-Y][Gd@C_{82}]$ (**13**) complexes, were investigated before. In this study, the first and second activation free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^\ddagger$ and

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k_{et} ($n = 1, 2$), respectively, which are given by the previous studies for $[X-UT-Y][Ce@C_{82}]$ (**12**) and $[X-UT-Y][Gd@C_{82}]$ (**13**) complexes, were calculated in accordance with the *Marcus* theory.

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1. Introduction

Carbon materials are found in a variety of forms, such as graphite, diamond, carbon fibers, fullerenes, and carbon nanotubes. The shapes of these nano-sized new carbon structures included perfect spheres, ellipsoids, tubes, fibers, polyhedra and further variations, all of them still conforming to the same structural principle as C_{60} (Psaras and Langford, 1987; Singh Nalwa et al., 2002; Ōsawa, 2002). Since the discovery of fullerenes (C_n), one of the main classes of carbon compounds, and the unusual structures and properties of these molecules, many potential applications and physicochemical properties have been discovered and introduced. At the present time, various empty carbon fullerenes with a different magic number “ n ” such as C_{20} , C_{60} , C_{70} , C_{80} , C_{180} , and C_{240} have been obtained. Endohedral metallofullerenes were first introduced as a new spherical fullerene group with unique properties (Ōsawa, 2002; Shen, 2007). One of the common structural molecules is the $M@C_{82}$ complex. Metallofullerenes are often characterized by the ‘charge-per-metal’ atom encapsulated. This description implies that the oxidation of the metal atom during metallofullerene formation drives the extent of charge transfer to the fullerene cage. Formation of endohedral metallofullerenes is thought to involve the transfer of electrons from the encapsulated metal atoms to the surrounding fullerene cage (Taherpour, 2008; Anderson et al., 2000; Weaver et al., 1992; Smalley, 1992). Significantly, C_{82} and C_{84} are known to form endohedral metallofullerenes. The possibility of a charge transfer reaction during metallofullerene formation is responsible, considering the relatively large electron affinities of the fullerene cages (Taherpour, 2008; Anderson et al., 2000; Weaver et al., 1992; Smalley, 1992; Yannoni et al., 1992). It also suggests that the electronic structure of the fullerene cage is an important parameter for the formation of metallofullerenes. The voltammetry of a series of C_{82} and C_{84} metallofullerenes was investigated by Anderson et al. (2000) in an attempt to understand their behavior in terms of the electronic structure.

The square-wave voltammetry for a series of related fullerenes and metallofullerenes measured in pyridine solutions containing 0.10 M tetra-*n*-butylammonium perchlorate is reported (Taherpour, 2008). Several dimetallic metallofullerenes, $M@C_x$, are found to have similar voltammetric responses regardless of metal identity or carbon number. Assignment of formal charges to the fullerene cage suggests that these metallofullerenes are isoelectronic and have related molecular orbital structures (Anderson et al., 2000). A variety of metallofullerenes having a C_{82} cage have been identified where either the type or the number of metal atoms within the C_{82} cage is altered (like $La@C_{82}$ and $Y@C_{82}$) (Anderson et al., 2000; Weaver et al., 1992). The symmetry of these metallofullerenes has not been characterized, but the voltammetry suggests that these species may have related electronic structures (Anderson et al., 2000; Stevenson et al., 1994). It was unexpected, however, to find a C_{82} or C_{84} metallofullerene having the appearance of related electronic structures. The $(Sc_2)^{+4}@C_{84}^{-4}$ formal

charges are assigned to the metallofullerene, in agreement with recent chromatographic results from Dorn (Anderson et al., 2000; Stevenson et al., 1994; Taherpour, 2008). The formal charges for $Er_2@C_{82}$ were assigned as $(Er_2)^{+6}@C_{82}^{-6}$ (Anderson et al., 2000; Slanina et al., 2004; Taherpour, 2008). The voltammetry of $Sc_2@C_{84}$ is nearly identical to that of $Er_2@C_{82}$, suggesting that the identity of the encapsulated metal ion does not influence the electronic structure of dimetallic metallofullerenes (DMFs). This result corresponds with reports in the literature for the electrochemistry of monometallic C_{82} metallofullerenes (e.g., $La@C_{82}$ and $Y@C_{82}$) (Nagase and Kobayashi, 1994; Kikuchi et al., 1994; Suzuki et al., 1996, 1993). Hoffman et al. show by emission measurements that Er exists as the “+3” cation in $Er_2@C_{82}$ (Anderson et al., 2000; Taherpour, 2008). Relative concentrations of nine isomers of $Ca@C_{82}$ derived from the C_{82} isolated-pentagon-rule satisfying cages have been computed over a wide temperature interval (Iiduka et al., 2006). The computations are based on the Gibbs energy constructed from partition functions supplied with molecular parameters from density functional theory calculations. Five structures show significant populations at higher temperatures: $C_{2v} > C_s > C_2 > C_{3v} > C_s$. The computed relative stabilities agree well with available observations. As for $Er@C_{82}$, it may be mentioned that minor isomers are likely analogous to $Ca@C_{82}$ (Iiduka et al., 2006). Determination of the charge-per-Sc atom of $Sc_2@C_{84}$ (**10**) by chromatography, however, suggests that the Sc atoms have a “+2” charge (Anderson et al., 2000; Fuchs et al., 1996).

In 1991, Smalley and his collaborators demonstrated that fullerene lanthanides can be produced by laser vaporization of graphite and lanthanum oxide and extracted by toluene (Fuchs et al., 1996; Bethune et al., 1993; Chai et al., 1991). The physical measurements, such as EPR (Fuchs et al., 1996; Johnson et al., 1992; Suzuki et al., 1992, 1993; Bandow et al., 1992; Hoinkis et al., 1992; Weaver et al., 1992; Shinohara et al., 1992; Kato et al., 1993), mass spectrometry (Fuchs et al., 1996; Alvarez et al., 1991; Ross et al., 1992; Gillan et al., 1992; Moro et al., 1993), extended X-ray absorption fine structure (EXAFS) (Fuchs et al., 1996; Soderholm et al., 1992; Park et al., 1993) and X-ray photoelectron spectroscopy (XPS) (Fuchs et al., 1996; Weaver et al., 1992), were performed on the extracts containing the mixture of fullerene lanthanides and empty fullerenes.

Unsaturated thiocrown ethers with *cis*-geometry (**1–9**) demonstrate interesting properties for physicochemical studies due to their conformational restriction compared to a corresponding saturated system and to the size of their cavities. The presence of sulfur atoms in the structure of crown ethers accounts for the different properties of thiocrown ethers. The *cis*-unsaturated thiocrown ethers **1–9** were synthesized, and their structures were confirmed (Taherpour, 2008; Tsuchiya et al., 2001, 2006; Cooper, 1988; Blake and Schröder, 1990; Cooper and Rawle, 1990; Parker, 1996; Pedersen, 1971; Murray and Hartley, 1981; Nakayama et al., 1999; Bojkova and Glass, 1998; Diener and Alford, 1998). 1,4-dithiin is the smallest member of compounds **1–9** to have been widely studied (Anderson

et al., 2000; Weaver et al., 1992; Smalley, 1992; Yannoni et al., 1992; Ruoff et al., 1995; Fowler and Manolopoulos, 1995; Hoffman et al., 1995; Dennis et al., 1998; Stevenson et al., 1994; Iiduka et al., 2006; Slanina et al., 2004; Nagase and Kobayashi, 1994). In 2001, the structures of $[X-UT-Y]$ ($X = 6, 9, 12, 15, 18, 21, 24$ and 27 ; $Y = 2-9$) **1-9** were reported by Tsuchiya et al. (2001). In that report, ^1H and ^{13}C NMR signals, X-ray crystallography and ORTEP drawings, cavity size, and UV spectral data of $[X-UT-Y]$ **1-9** were considered carefully (Tsuchiya et al., 2001). In 2006, the oxidation potential ($^{\text{ox}}E_1$), cyclic voltammetry (Fc/Fc^+), and the free energy of electron transfer (ΔG_{et}) of the supramolecular complex of $[X-UT-Y][\text{C}_{60}]$ and $[X-UT-Y][\text{La}@\text{C}_{82}]$ of *cis*-unsaturated thiocrown ethers **1-9** were considered by Tsuchiya et al. (2006). The endohedral metallofullerenes and complexes with the thiocrown ethers have shown interesting properties for applications and studies. In 2006, the oxidation potential ($^{\text{redox}}E_1$) of $\text{Sc}_2@\text{C}_{84}$ (**10**) and $\text{Er}_2@\text{C}_{82}$ (**11**) were reported by Anderson et al. (2000).

Graph theory has been found to be a useful tool in *QSAR* (Quantitative Structure Activity Relationship) and *QSPR* (Quantitative Structure Property Relationship) (Hansen and Jurs, 1988; Hosoya, 1971; Randić, 1998, 1975; Rücker and Rücker, 1999; Wiener, 1947; Du et al., 2002). Numerous studies have been performed related to the abovementioned fields by using the so-called topological indices (TIs) Randić, 1975; Slanina et al., 1997; Playšić et al., 1993; Rehm and Weller, 1970; Taherpour, 2008. In 1993 and 1997, a related complex of applications of the Wiener and Harary indices in fullerene science was reported (Slanina et al., 1997; Playšić et al., 1993).

The use of effective mathematical methods to suitably correlate between several data properties of chemicals is important. The ratio of the summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers (μ_{cs}) was a useful numerical and structural value of the unsaturated thiocrown ethers **1-9** that were utilized here.

In Fig. 1 was shown the structures of unsaturated thiocrown ethers **1-9** with **10** and **11**, to produce supramolecular complexes $[X-UT-Y][\text{M}@\text{C}_{82}]$ ($\text{M} = \text{Ce}$ and Gd) **12** and **13**.

In this work, the first and second activation free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^\ddagger$ and k_{et} ($n = 1, 2$), respectively, on the basis of the previous studies for $[X-UT-Y][\text{Ce}@\text{C}_{82}]$ (**12**) and $[X-UT-Y][\text{Gd}@\text{C}_{82}]$ (**13**) complexes, were calculated in accordance with the Marcus theory. The QSAR studies of this index relative to some of the structural data of thiocrown ethers **1-9**,

their maximum wavelength (λ_{max}), cavity size, and oxidation potential ($^{\text{ox}}E_1$), as well as the free energy of electron transfer (ΔG_{et}) between **1-9** and C_{60} and $\text{La}@\text{C}_{82}$, $\text{Sc}_2@\text{C}_{84}$, $\text{Er}_2@\text{C}_{82}$, $\text{Ce}@\text{C}_{82}$ and $\text{Gd}@\text{C}_{82}$ were reported previously (Rehm and Weller, 1970; Taherpour, 2007a,b, 2008, 2010).

2. Graphs and mathematical method

All mathematical and graphing operations were performed using *MATLAB-7.4.0(R2007a)* and *Microsoft Office Excel-2003* programs. The ratio of the sum of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers (μ_{cs}) is a useful numerical and structural value for the unsaturated thiocrown ethers **1-9** that were investigated (Rehm and Weller, 1970; Taherpour, 2007b, 2008, 2010).

$$\mu_{cs} = n_s + n_c / (n_s \cdot n_c) \quad (1)$$

If $n_c = 2n_s$, the coefficient of μ_{cs} is given by

$$\mu_{cs} = 3 / (2n_s) \quad (2)$$

For modeling, both linear (MLRs: Multiple Linear Regressions) and nonlinear (ANN: Artificial Neural Network) models were examined in this study. Other indices were examined and the best results and equations for extending the physico-chemical and electrochemical data were chosen.

The Rehm-Weller equation estimates the free energy change between an electron donor (*D*) and an acceptor (*A*) as: Rehm and Weller, 1970

$$\Delta G_{et}^\circ = e[E_D^\circ - E_A^\circ] - \Delta E^* + \omega_1 \quad (3)$$

where “*e*” is the unit electrical charge, E_D° and E_A° are the reduction potentials of the electron donor and acceptor, respectively, ΔE^* is the energy of the singlet or triplet excited state, and ω_1 is the work required to bring the donor and acceptor within the electron transfer (ET) distance. The work term in this expression can be considered to be ‘0’ in so far as there exists an electrostatic complex before the electron transfer (Rehm and Weller, 1970).

Marcus theory of electron transfer implies rather weak (< 0.05 eV) electronic coupling between the initial (locally excited, LE) and final (electron transfer, CT) states and presumes that the transition state is close to the crossing point of the LE and CT terms. The value of the electron transfer rate constant k_{et} is controlled by the activation free energy ΔG_{et}^\ddagger , which is a function of the reorganization energy ($l/4$) and electron transfer driving force ΔG_{et} (Marcus, 1993, 1965; Andrea, 2008; Barbara, 1996; Newton, 1991; Jortner and Freed, 1970; Marcus and Sutin, 1985; Kuzmin, 2000):

$$\Delta G_{et}^\ddagger = (l/4)(1 + \Delta G_{et}/l)^2 \quad (4)$$

$$k_{et} = k_0 \exp(-\Delta G_{et}^\ddagger/RT) \quad (5)$$

For organic molecules, the reorganization energy was found to be in the range of 0.1–0.3 eV. In this study, the minimum amount of reorganization energy was used (Marcus, 1993, 1965; Andrea, 2008; Barbara, 1996; Newton, 1991; Jortner and Freed, 1970; Marcus and Sutin, 1985; Kuzmin, 2000).

3. Discussion

The relationships between “ μ_{cs} ” index and oxidation potential ($^{\text{ox}}E_1$) of **1-9**, as well as the first and second free energies of

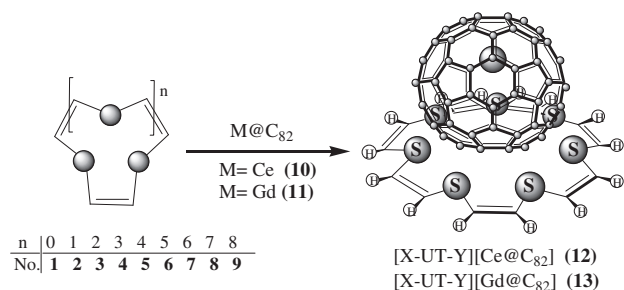


Figure 1 The total structures of unsaturated thiocrown ethers **1-9**, their supramolecular complexes of $[X-UT-Y][\text{Ce}@\text{C}_{82}]$ (**12**) & $[X-UT-Y][\text{Gd}@\text{C}_{82}]$ (**13**).

electron transfer ($\Delta G_{et(n)}$, for $n = 1, 2$; which is given by the Rehm–Weller equation) between **1–9** and $\text{Ce}@C_{82}$ (**10**) and $\text{Gd}@C_{82}$ (**11**) and their supramolecular complex derivatives as $[X\text{--}UT\text{--}Y][M@C_{82}]$ ($M = \text{Ce}$ and Gd) **12** and **13** were presented and investigated before (Taherpour, 2010). It was reported that each of the metallofullerenes has a remarkably small potential difference between the first oxidation and the first reduction (Suzuki et al., 1996). This may suggest that the HOMO of $M@C_{82}$, originally the LUMO⁺ of the C_{82} , is singly occupied (i.e., SOMO) as purposed for $\text{La}@C_{82}$ (Suzuki et al., 1996). The ionization potential, electron affinity, oxidation and reduction potentials of $\text{Ce}@C_{82}$ and $\text{Gd}@C_{82}$ (E in volts vs. Fc/Fc^+ and radii of lanthanides) were reported previously. It was found that the ionic radii of Ln^{3+} show good linear relationships with the first redox potentials (Suzuki et al., 1996). The ionization potentials and electron affinities of $M@C_{82}$ ($M = \text{lanthanides}$) were reported as obtained by ab initio calculations (Suzuki et al., 1996; Nagase and Kobayashi, 1994). The first oxidation and reduction processes occur on the SOMO whose electron density is higher on the cage close to the M^{3+} ($M = \text{lanthanides}$) Suzuki et al., 1996; Nagase and Kobayashi, 1994; Laasonen et al., 1992. The electrons on the SOMO are bound to the cage with a higher energy when the metal–carbon distance decreases because the electrostatic interactions between electrons and the metal intensify (Suzuki et al., 1996). Several important metallofullerenes, $M@C_{82}$ (where $M = \text{Ce}$ and Gd), were found to have similar voltammetric responses regardless of metal identity or carbon number. Assignment of formal charges to the fullerene cage (that they are characterized by the ‘charge-per-metal’ atom encapsulated) suggests that these metallofullerenes are isoelectronic and have related molecular orbital structures (Anderson et al., 2000). The predicted complex structures of unsaturated thiocrown ethers (**1–9**) with **10** and **11** were introduced here as $[X\text{--}UT\text{--}Y][\text{Ce}@C_{82}]$ (**12**) and $[X\text{--}UT\text{--}Y][\text{Gd}@C_{82}]$ (**13**) complexes. The potential difference between the oxidation and reduction in these structures is related to the band gap of HOMO–LUMO orbitals. The electronic properties of $\text{Ce}@C_{82}$ and $\text{Gd}@C_{82}$ are very similar to those of $\text{La}@C_{82}$, although both Ce and Gd have 4f level electrons. It was suggested that these 4f electrons do not play an important role in fullerenolanthanide chemistry as seen in organic and inorganic lanthanide chemistry (Suzuki et al., 1996; Nagase and Kobayashi, 1993; Marks and Ernst, 1982; Cotton and Wilkinson, 1988).

The X-ray crystal structures and ORTEP drawings for some of the structures of **1–9** $[X\text{--}UT\text{--}Y]$ ($X = 15, 18, 21, 24$ and 27 ; $Y = 5\text{--}9$) were determined. These show there are cavities in these molecules, and also that the sulfur atoms are nearly coplanar (Tsuchiya et al., 2001). The average radii of the cavity sizes for **4–8** are 1.76, 2.34, 3.48, 4.43 and 5.36 Å, respectively (Fowler and Manolopoulos, 1995; Tsuchiya et al., 2001, 2006). The ^{13}C and ^1H NMR results (in CDCl_3) were reported previously. These results show that compound **4** has the highest chemical shifts in both ^1H and ^{13}C NMR. The electron density of the $\text{C}=\text{C}$ increases with the size of the rings from **4** → **9** and diminishes from **4** → **1** with decreasing ring size of $[X\text{--}UT\text{--}Y]$ (Tsuchiya et al., 2001, 2006). The first and second reduction potentials ($^{red}E_1$) of $\text{Ce}@C_{82}$ (**10**) are -0.41 and -1.41 V, and, for $\text{Gd}@C_{82}$ (**11**), they are -0.39 and -1.38 V, respectively (Suzuki et al., 1996). The oxidation potentials ($^{ox}E_1$) of **4–7** were measured to be 0.82, 0.79, 0.73 and 0.69 V, respectively

(Anderson et al., 2000; Tsuchiya et al., 2001, 2006). The free energies of electron transfer (ΔG_{et}) between **1–9** with **10** and/or **11** to produce $[X\text{--}UT\text{--}Y][\text{Ce}@C_{82}]$ (**12**) and $[X\text{--}UT\text{--}Y][\text{Gd}@C_{82}]$ (**13**) complexes were calculated by the Rehm–Weller equation (Anderson et al., 2000; Weaver et al., 1992; Park et al., 1993; Rehm and Weller, 1970; Taherpour, 2007b, 2008).

Table 1 has shown the *Nieperian* logarithmic behavior equations (6–9) that indicate the relationship between the index μ_{cs} and the first and second free energies of the free activated electron transfer ($\Delta G_{et(n)}^\ddagger$, $n = 1, 2$) between unsaturated thiocrown ethers **1–9** with **10** and **11** in the structures $[X\text{--}UT\text{--}Y][M@C_{80\text{--}R}]$ ($M = \text{Ce}$ & Gd) **12** and **13**. In Table 1 was shown the very good R^2 of the relationships.

The values of the relative data of **1–9** are shown in Table 2. The values shown in Table 2 demonstrate that μ_{cs} decreases with increasing molecular size of the compounds **1–9**. In Table 2, the related values for the supramolecular complexes of $[X\text{--}UT\text{--}Y]$ **1–9** with $\text{Ce}@C_{84}$ (**10**) and $\text{Gd}@C_{82}$ (**11**) are also shown. Table 2 shows the values of oxidation potential ($^{ox}E_1$), as well as the free energy of electron transfer ($\Delta G_{et(n)}^\ddagger$; $n = 1, 2$) between some of the $[X\text{--}UT\text{--}Y]$ and their complexes with **10** and **11**.

In Table 3 was shown the calculated values of the first and second kinetic rate constants of the electron transfers (k_{et}) between unsaturated thiocrown ethers **1–9** with **10** and **11** in the structures of $[X\text{--}UT\text{--}Y][\text{Ce}@C_{82}]$ (**12**) and $[X\text{--}UT\text{--}Y][\text{Gd}@C_{82}]$ (**13**) complexes.

In Fig. 2, two-dimensional diagram shows the relationships between the main values that were demonstrated in Table 1.

The ratio of summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers (μ_{cs}) shows a high correlation with the physicochemical and structural values of the unsaturated thiocrown ethers **1–9**. The results show the calculated values of free energy of electron transfer (ΔG_{et}) of the $[X\text{--}UT\text{--}Y][\text{Ce}@C_{82}]$ (**12**) and $[X\text{--}UT\text{--}Y][\text{Gd}@C_{82}]$ (**13**) supramolecular complexes on the basis of the first and second reduction potentials ($^{red}E_1$ and $^{red}E_2$) of $\text{Ce}@C_{82}$ (**10**) and $\text{Gd}@C_{82}$ (**11**). The data for the compounds and their complexes were previously reported (Taherpour, 2010).

Marcus theory is currently the dominant theory of electron transfer in chemistry. Marcus theory is so widely accepted because it makes surprising predictions about electron transfer rates that have been nonetheless supported experimentally over the last several decades (Marcus, 1993, 1965; Andrea, 2008; Barbara, 1996; Newton, 1991; Jortner and Freed, 1970; Marcus and Sutin, 1985; Kuzmin, 2000).

Electron transfer (ET) is one of the most important chemical processes in nature, playing a central role in many biological, physical and chemical (both organic and inorganic) systems. Solid state electronics depend on the control of the ET in semiconductors, and the new area of molecular electronics depends critically on the understanding and the control of the transfer of electrons in and between molecules and nanostructures. The other reason to study electron transfer is that it is a very simple kind of chemical reaction and in understanding it, one can gain insight into other kinds of chemistry and biochemistry. After all, what is important is the chemistry of the transfer of electrons from one place to another (Marcus, 1993, 1965; Andrea, 2008; Barbara, 1996; Newton, 1991; Jortner and Freed, 1970; Marcus and Sutin, 1985; Kuzmin, 2000).

Table 1 The *Nieperian* logarithmic behavior equations (6–9) that indicate the relationship between the index μ_{cs} and the first and second free energies of the free activated electron transfer ($\Delta G_{et(n)}^\ddagger$, $n = 1, 2$) between unsaturated thiocrown ethers **1–9** with **10** and **11** in the structures $[X-UT-Y][M@C_{80-R}]$ ($M = Ce \& Gd$) **12** and **13**.

Equations	$[X-UT-Y][M@C_{82}]$ $M = Ce, Gd$	n	R^2	$\Delta G_{et(n)}^\ddagger = aLn(n) + b$	
				a	b
Eq. (6)	$[X-UT-Y][Ce@C_{82}]$	1	0.989	11.79	51.21
Eq. (7)	$[X-UT-Y][Ce@C_{82}]$	2	0.984	19.38	120.60
Eq. (8)	$[X-UT-Y][Gd@C_{82}]$	1	0.989	11.65	50.14
Eq. (9)	$[X-UT-Y][Gd@C_{82}]$	2	0.987	18.91	118.00

Table 2 The values of data coefficients of unsaturated thiocrown ethers $[X-UT-Y]$ **1–9** and the values of the activation free energies of electron transfer (ΔG_{et}^\ddagger) in kcal mol^{-1} between unsaturated thiocrown ethers **1–9** with $[X-UT-Y][Ce@C_{82}]$ (**12**) and $[X-UT-Y][Gd@C_{82}]$ (**13**) complexes. The first and second reduction potentials (${}^{red}E_1$) of $Ce@C_{82}$ (**10**) are -0.41 and -1.41 V, respectively, and of $Gd@C_{82}$ (**11**) are -0.39 and -1.38 V, respectively. See reference (Taherpour, 2010).

No.	Formula of ^a $[X-UT-Y]$	n_s	n_c	μ_{cs}	${}^{ox}E_1$ (Volt)	ΔG_{et}^\ddagger (kcal mol^{-1}) First redox. $[X-UT-Y][Ce@C_{82}]$ (12) complexes	ΔG_{et}^\ddagger (kcal mol^{-1}) second redox. $[X-UT-Y][Ce@C_{82}]$ (12) complexes	ΔG_{et}^\ddagger (kcal mol^{-1}) First redox. $[X-UT-Y]$ $[Gd@C_{82}]$ (13) complexes	ΔG_{et}^\ddagger (kcal mol^{-1}) second redox. $[X-UT-Y]$ $[Gd@C_{82}]$ (13) complexes
1	6-UT-2 (1,4-dithiin)	2	4	0.7500	1.02	46.69	112.98	45.65	110.57
2	9-UT-3	3	6	0.5000	0.97	44.14	108.99	43.13	106.63
3	12-UT-4	4	8	0.3750	0.89	40.18	102.75	39.25	100.43
4	15-UT-5	5	10	0.3000	0.82	36.79	97.42	35.97	95.19
5	18-UT-6	6	12	0.2500	0.79	35.59	95.19	34.62	92.98
6	21-UT-7	7	14	0.2143	0.73	32.47	90.81	31.98	88.62
7	24-UT-8	8	16	0.1875	0.69	31.13	86.50	30.29	85.79
8	27-UT-9	9	18	0.1667	0.66	29.88	85.79	29.05	83.70
9	30-UT-10	10	20	0.1500	0.63	28.65	83.70	27.84	81.64

^a The data for the compounds and their complexes have not been previously reported. $[X-UT-Y][Ce@C_{82}]$ (**12**) and $[X-UT-Y][Gd@C_{82}]$ (**13**) supramolecular complexes were not synthesized before.

Table 3 The values of the first and second kinetic rate constants of the electron transfers (k_{et}) between unsaturated thiocrown ethers **1–9** with **10** and **11** in $[X-UT-Y][Ce@C_{82}]$ (**12**) and $[X-UT-Y][Gd@C_{82}]$ (**13**) complexes.

No.	Formula of ^a $[X-UT-Y]$	n_s	n_c	μ_{cs}	${}^{ox}E_1$ (Volt)	k_{et} (kcal mol^{-1}) first redox. $[X-UT-Y]$ $[Ce@C_{82}]$ (12) complexes	k_{et} (kcal mol^{-1}) second redox. $[X-UT-Y][Ce@C_{82}]$ (12) complexes	k_{et} (kcal mol^{-1}) first redox. $[X-UT-Y]$ $[Gd@C_{82}]$ (13) complexes	k_{et} (kcal mol^{-1}) second redox. $[X-UT-Y]$ $[Gd@C_{82}]$ (13) complexes
1	6-UT-2 (1,4-dithiin)	2	4	0.7500	1.02	3.31×10^{-22}	7.91×10^{-71}	1.88×10^{-21}	4.57×10^{-69}
2	9-UT-3	3	6	0.5000	0.97	2.46×10^{-20}	6.66×10^{-68}	1.33×10^{-19}	3.58×10^{-66}
3	12-UT-4	4	8	0.3750	0.89	1.96×10^{-17}	2.48×10^{-63}	2.42×10^{-17}	1.25×10^{-61}
4	15-UT-5	5	10	0.3000	0.82	6.00×10^{-15}	2.04×10^{-59}	2.38×10^{-14}	8.80×10^{-58}
5	18-UT-6	6	12	0.2500	0.79	5.10×10^{-14}	8.80×10^{-58}	2.32×10^{-13}	3.63×10^{-56}
6	21-UT-7	7	14	0.2143	0.73	4.53×10^{-12}	1.44×10^{-54}	2.00×10^{-11}	5.74×10^{-53}
7	24-UT-8	8	16	0.1875	0.69	8.44×10^{-11}	2.08×10^{-51}	3.48×10^{-10}	6.82×10^{-51}
8	27-UT-9	9	18	0.1667	0.66	7.03×10^{-10}	6.82×10^{-51}	2.81×10^{-9}	2.33×10^{-49}
9	30-UT-10	10	20	0.1500	0.63	5.60×10^{-9}	2.33×10^{-49}	2.18×10^{-8}	7.64×10^{-48}

^a The data for the compounds and their complexes have not been previously reported. $[X-UT-Y][Ce@C_{82}]$ (**12**) and $[X-UT-Y][Gd@C_{82}]$ (**13**) supramolecular complexes were neither synthesized nor reported.

The free energy of electron transfer ΔG_{et} is the difference between the reactants on the left and the products on the right, and ΔG_{et}^\ddagger is the activation energy. The reorganization energy is

the energy it would take to force the reactants to have the same nuclear configuration as the products without permitting the electron transfer. If the entropy changes are ignored, the free

energy becomes energy or potential energy (Marcus, 1993, 1965; Andrea, 2008; Barbara, 1996; Newton, 1991; Jortner and Freed, 1970; Marcus and Sutin, 1985; Kuzmin, 2000).

Using Eqs. (4) and (5), it is possible to calculate the first and second activation free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^\ddagger$ and $k_{et(n)}$ ($n = 1-2$), respectively, for **12** and **13** in accordance with the Marcus theory. Fig. 3 shows the surfaces of the free energies of electron transfer $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^\ddagger$ ($n = 1-2$) between $[X-UT-Y]$ **1-9** with **10** and **11**, to produce supramolecular complexes $[X-UT-Y][M@C_{82}]$ ($M = Ce$ and Gd) **12** and **13**. The values of the first and second activation free energies of electron

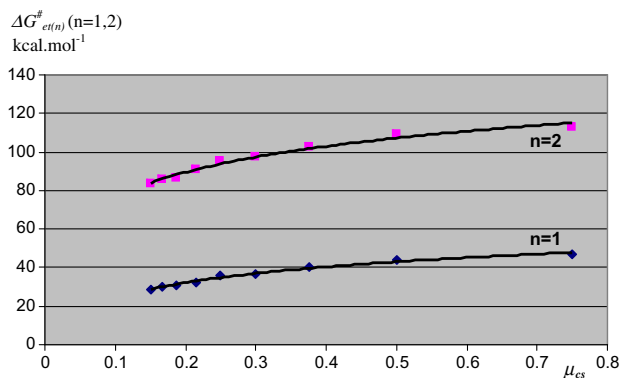


Figure 2 The relationship of μ_{cs} versus the first and second free activated energies of electron transfer ($\Delta G_{et(n)}^\ddagger$; $n = 1,2$ in kcal mol⁻¹) between **1-9** and the Ce@C₈₂ (**10**) for $[X-UT-Y][Ce@C_{82}]$ (**12**) supramolecular complexes are shown. The structure of the relationship of μ_{cs} versus the first and second free activated energies of electron transfer ($\Delta G_{et(n)}^\ddagger$; $n = 1,2$ in kcal mol⁻¹) between **1-9** and the Gd@C₈₂ (**11**) for $[X-UT-Y][Gd@C_{82}]$ (**13**) supramolecular complexes have same behavior as shown in Fig. 2.

transfer, $\Delta G_{et(n)}^\ddagger$ ($n = 1-2$) for **12** and **13**, decrease with $\Delta G_{et(n)}$ and μ_{cs} descriptor, while the kinetic rate constants of the electron transfers $k_{et(n)}$ ($n = 1-2$), increase with decreasing $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^\ddagger$ ($n = 1-2$) for **12** and **13** complexes. See Tables 2 and 3 and Fig. 3.

Fig. 3 shows the surfaces of the free energies of electron transfer $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^\ddagger$ ($n = 1$ and 2) between **1-9** with **10** and **11** in the structures **12** and **13** complexes. With the appropriate equations and in light of the good correlations (see Figs. 1-3 and equations 1-9), it is possible to calculate the values of the first and second free energies of electron transfer (ΔG_{et} in kcal mol⁻¹), the first and second activation free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^\ddagger$ and $k_{et(n)}$ ($n = 1-2$), respectively, for **12** and **13**, in close accordance with the results of Marcus theory. The supramolecular complexes of unsaturated thio-crown ethers **1-9** with **10** and **11** as $[X-UT-Y][M@C_{82}]$ ($M = Ce$ and Gd) **12** and **13** and their electrochemical data $\Delta G_{et(n)}^\ddagger$ and $k_{et(n)}$ ($n = 1,2$) have neither been synthesized nor reported before. But the first and second free energies of electron transfer ($\Delta G_{et(n)}$, for $n = 1,2$; which were given by the Rehm-Weller equation) between **1-9** and Ce@C₈₂ (**10**) and Gd@C₈₂ (**11**) and their supramolecular complexes derivatives as $[X-UT-Y][M@C_{82}]$ ($M = Ce$ and Gd) **12** and **13** were presented and investigated before (Taherpour, 2010).

4. Conclusion

Fullerene C₈₂ is known to readily form endohedral metallofullerenes. Formation of endohedral metallofullerenes is thought to involve the transfer of electrons from the encapsulated metal atom(s) to the surrounding fullerene cage. The *cis*-UT ethers **1-9** have important physicochemical properties. The electrochemical behaviors, oxidation potential (^{ox}E₁) and the free energies of electron transfer (ΔG_{et}) on the basis of the first and second reduction potentials (^{red}E₁ and ^{red}E₂) of Ce@C₈₂ (**10**) and Gd@C₈₂ (**11**) for the predicted supramolecular complexes of

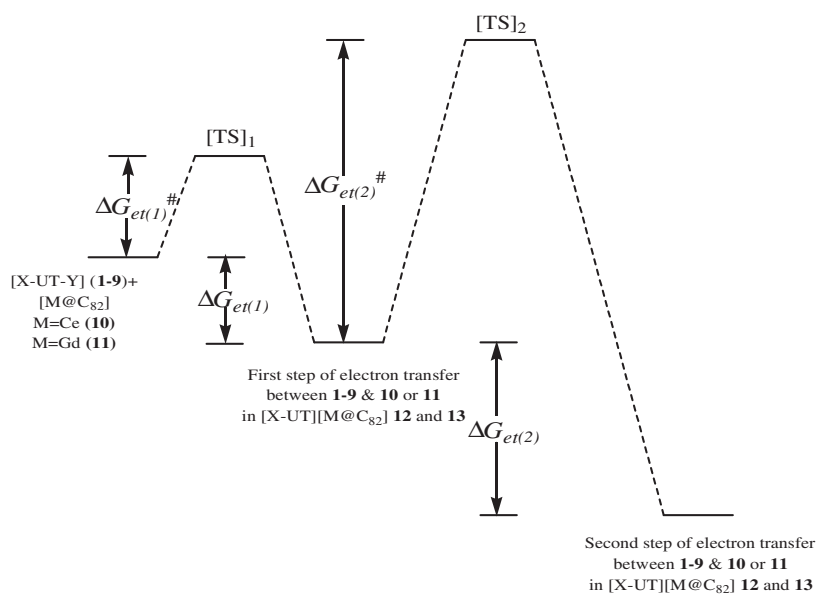


Figure 3 The surfaces of the free energies of electron transfer $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^\ddagger$ ($n = 1,2$) for **1-9** with **10** and **11** in the structures of $[X-UT-Y][M@C_{82}]$ ($M = Ce$ and Gd) **12** and **13**. For the data of $\Delta G_{et(n)}$ ($n = 1,2$) see reference (Taherpour, 2010).

$[X-UT-Y][Ce@C_{82}]$ (**12**) and $[X-UT-Y][Gd@C_{82}]$ (**13**) were reported before. The predicted values of ΔG_{et} for **12** and **13** were calculated by using the Rehm–Weller equation. Using the ratio of summation of the number of carbon atoms (n_c) and the number of sulfur atoms (n_s) to the product of these two numbers (μ_{cs}), the equations of the model can derive sound structural relationships between the aforementioned physicochemical data. By utilizing the model, one can calculate the values $\Delta G_{et(n)}$ ($n = 1-2$), $\Delta G_{et(n)}^\ddagger$ and $k_{et(n)}$ ($n = 1-2$) on the basis of the first and second reduction potentials (${}^{red}E_1$ and ${}^{red}E_2$) of **10** and **11** for the **12** and **13** supramolecular complex groups using the Rehm–Weller equation and Eqs. (2), (3) concerning the Marcus theory. The compounds $[X-UT-Y][Ce@C_{82}]$ (**12**) and $[X-UT-Y][Gd@C_{82}]$ (**13**) supramolecular complexes were previously neither synthesized nor reported.

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References

- Alvarez, M.M., Gillan, E.G., Holczer, K., Kaner, R.B., Min, K.S., Whetten, R.L., 1991. *J. Phys. Chem.* 95, 10561.
- Anderson, M.R., Dorn, H.C., Stevenson, S.A., 2000. *Carbon* 38, 1663–1670 (and the literature cited therein).
- Andrea Marcus, M., 2008. Theory for Electron Transfer a short introduction MPIP-Journal Club-Mainz-January 29.
- Bandow, S., Kitagawa, H., Mitani, T., Inokuchi, H., Saito, Y., Yamaguchi, H., Hayashi, N., Sato, H., Shinohara, H., 1992. *J. Phys. Chem.* 96, 9609.
- Barbara, P.F., 1996. *J. Phys. Chem.* 100, 13148–13161.
- Bethune, D.S., Johnson, R.D., Salem, J.R., de Vries, M.S., Yannoni, C.S., 1993. *Nature* 366, 123.
- Blake, A.J., Schröder, M., 1990. *Adv. Inorg. Chem.* 35, 1.
- Bojkova, N.V., Glass, R.S., 1998. *Tetrahedron Lett.* 39, 9125 (and the literature cited therein).
- Chai, Y., Guo, T., Jin, C., Haufler, R.E., Chibante, L.P.F., Fure, J., Wang, L., Alford, J.M., Smalley, R.E., 1991. *J. Phys. Chem.* 95, 7564.
- Cooper, S.R., 1988. *Acc. Chem. Res.* 21, 141.
- Cooper, S.R., Rawle, S.C., 1990. *Struct. Bonding* 72, 1.
- Cotton, F.A., Wilkinson, G., 1988. *Advanced Inorganic Chemistry*. John Wiley & Sons, New York (Chapter 20).
- Dennis, T.J.S., Kai, T., Tomiyama, T., Shinohara, H., 1998. *Chem. Commun.*, 619–620.
- Diener, M.D., Alford, J.M., 1998. *Nature* 393 (6686), 668–671.
- Du, Y.P., Liang, Y.Z., Li, B.Y., Xu, C.J., 2002. *J. Chem. Inf. Comput. Sci.* 42, 1128–1138.
- Fowler, P.W., Manolopoulos, D.E., 1995. In: *An Atlas of Fullerenes*, vol. 30. Clarendon Press, Oxford.
- Fuchs, D., Rietschel, H., Michel, R.H., Fischer, A., Weis, P., Kappes, M.M., 1996. *J. Phys. Chem.* 100 (2), 725–729.
- Gillan, E.G., Yerezian, C., Min, K.S., Alvarez, M.M., Whetten, R.L., Kaner, R.B., 1992. *J. Phys. Chem.* 96, 6869.
- Hansen, P.J., Jurs, P., 1988. *J. Chem. Edu.* 65, 574–580 (and the literature cited therein).
- Hoffman, K.R., Delapp, K., Andrews, H., Sprinkle, P., Nickels, M., Norris, B., 1995. *J. Lumin.* 66–67 (1–6), 244–248.
- Hoinkis, M., Yannoni, C.S., Bethune, D.S., Salem, J.R., Johnson, R.D., Crowder, M.S., Vries, De, 1992. *Chem. Phys. Lett.* 198, 461.
- Hosoya, H., 1971. *Bull. Chem. Soc. Jpn.* 44, 2332–2339.
- Iiduka, Y., Wakahara, T., Nakajima, K., Tsuchiya, T., Nakahodo, T., Maeda, Y., Akasaka, T., Mizorogi, N., Nagase, S., 2006. *Chem. Commun.*, 2057–2059.
- Johnson, R.D., de Vries, M.S., Salem, J., Bethune, D.S., Yannoni, C.S., 1992. *Nature* 355, 239.
- Jortner, J., Freed, K.F., 1970. *J. Chem. Phys.* 52, 6272–6291.
- Kato, T., Suzuki, S., Kikuchi, K., Achiba, Y., 1993. *J. Phys. Chem.* 97, 13425.
- Kikuchi, K., Nakao, Y., Suzuki, S., Achiba, Y., 1994. *J. Am. Chem. Soc.* 116 (20), 9367–9368.
- Kuzmin, M.G., 2000. XVIIth IUPAC Symposium on Photochemistry. Dresden, German, July 22–27, 2000, Book of Abstracts. p. 372.
- Laasonen, K., Andreoni, W., Parrinello, M., 1992. *Science* 1916, 258.
- Marcus, R.A., 1965. *J. Chem. Phys.* 43, 679.
- Marcus, R.A., 1993. *Rev. Mod. Phys.* 65 (3), 599–610.
- Marcus, R.A., Sutin, N., 1985. *Biochim. Biophys. Acta.* 811, 265.
- Marks, T.J., Ernst, R.D., 1982. In: Wilkinson, G., Stone, F.G.A., Abel, E.W. (Eds.), *Comprehensive Organometallic Chemistry*. Pergamon Press, Oxford (Chapter 21).
- Moro, L., Ruoff, R.S., Becker, C.H., Lorents, D.C., Malhotra, R., 1993. *J. Phys. Chem.* 97, 6801.
- Murray, S.G., Hartley, F.R., 1981. *Chem. Rev.* 81, 365.
- Nagase, S., Kobayashi, K., 1993. *Chem. Phys. Lett.* 214, 57.
- Nagase, S., Kobayashi, K., 1994. *Chem. Phys. Lett.* 231 (2–3), 319–324.
- Nagase, S., Kobayashi, K., 1994. *J. Chem. Soc., Chem. Commun.*, 1837.
- Nakayama, J., Kaneko, A., Sugihara, Y., Ishii, A., 1999. *Tetrahedron* 55, 10057.
- Newton, M.D., 1991. *Chem. Rev.* 91, 767–792.
- Eiji Ōsawa, 2002. Perspectives of Fullerene Nanotechnology. In: Eiji Ōsawa (Ed.), first ed. Nanocarbon Research Institute, Chiba, Japan KLUWER ACADEMIC PUBLISHERS NEW YORK, BOSTON, DORDRECHT, LONDON, MOSCOW.
- Park, C.-H., Wells, B.O., DiCarlo, J., Shen, Z.-X., Salem, J.R., Bethune, D.S., Yannoni, C.S., Johnson, R.D., de Vries, M.S., Booth, C., Bridge, F., Pianetta, P., 1993. *Chem. Phys. Lett.* 213, 196.
- Parker, D. (Ed.), 1996. *Macrocyclic Synthesis: A Practical Approach*. Oxford University Press, New York.
- Pedersen, C.J., 1971. *J. Org. Chem.* 36, 254.
- Plavšić, D., Nikolić, S., Trinajstić, N., Mihalić, Z., 1993. *J. Math. Chem.* 12, 235–250.
- Psaras, P.A., Langford, H.D. (Eds.), 1987. *Advancing Materials Research*, U.S. National Academy of Engineering and National Academy of Sciences. National Academy Press, Washington, DC. p. 203.
- Randić, M., 1975. *J. Am. Chem. Soc.* 97, 6609–6615.
- Randić, M., 1998. *Acta Chim. Slov.* 45, 239–252.
- Rehm, D., Weller, A., 1970. *Isr. J. Chem.* 8, 259.
- Ross, M.M., Nelson, H.H., Callahan, J.H., McElvany, S.W., 1992. *J. Phys. Chem.* 96, 5231.
- Rücker, G., Rücker, C., 1999. *J. Chem. Inf. Comput. Sci.* 39, 788–802.
- Ruoff, R.S., Kadish, K.M., Bouslas, P., Chen, E.C.M., 1995. *J. Phys. Chem.* 99 (21), 8843–8850.
- Shen, H., 2007. *Mol. Phys.* 105 (17–18), 2405–2409.
- Shinohara, H., Sato, H., Saito, Y., Ohkohchi, M., Ando, Y., 1992. *J. Phys. Chem.* 96, 3571.
- Singh Nalwa, H., 2002. *Nanostructured Materials and Nanotechnology—Concise Edition*, Edited by H. Singh Nalwa, Hitachi Research Laboratory, Hitachi Ltd., Ibaraki, Japan, ACADEMIC PRESS, A Harcourt Science and Technology Company, second ed. San Diego San Francisco New York Boston London Sydney Tokyo.
- Slanina, Z., Chao, M.-C., Lee, S.-L., Gutman, I., 1997. *J. Serb. Chem. Soc.* 62 (3), 211–217.
- Slanina, Z., Kobayashi, K., Nagase, S., 2004. *J. Chem. Phys.* 120, 3397–3400.

- Smalley, R.E., 1992. In: Hamond, G.S., Kuck, V.J. (Eds.), *Fullerenes*. American Chemical Society, Washington DC, pp. 141–159.
- Soderholm, L., Wurz, P., Lykke, K.R., Parker, D.H., Lytle, F.W., 1992. *J. Phys. Chem.* 96, 7153.
- Stevenson, S., Dorn, H.C., Burbank, P.M., Harich, K., Haynes, J., Kiang, C.H., Salem, J.R., de Vries, M.S., van Loosdrecht, P.H.M., Johnson, R.D., Yannoni, C.S., Bethune, D.S., 1994. *Anal. Chem.* 66 (17), 2675–2679.
- Suzuki, S., Kawata, S., Shiromaru, H., Yamauchi, K., Kikuchi, K., Kato, T., Achiba, Y., 1992. *J. Phys. Chem.* 96, 7159.
- Suzuki, T., Maruyama, Y., Kato, T., Kikuchi, K., Achiba, Y., 1993. *J. Am. Chem. Soc.* 115 (23), 11006–11007.
- Suzuki, T., Kikuchi, K., Oguri, F., Nakao, Y., Suzuki, S., Achiba, Y., Yamamoto, K., Funasaka, H., Takahashi, T., 1996. *Tetrahedron* 52 (14), 4973–4982 (and the literature cited therein).
- Taherpour, A.A., 2007a. *Fullerenes, Nanotubes, Carbon Nanostruct.* 15, 279–289.
- Taherpour, A.A., 2007b. *Fullerenes, Nanotubes, Carbon Nanostruct.* 15, 405–415.
- Taherpour, A.A., 2008. *Fullerenes, Nanotubes Carbon Nanostruct.* 16, 196–205.
- Taherpour, A.A., 2008. *Fullerenes, Nanotubes, Carbon Nanostruct.* 16, 142–153.
- Taherpour, A.A., 2010. *Phosphorus, Sulfur, Silicon* 185, 422–432.
- Tsuchiya, T., Shimizu, T., Kamigata, N., 2001. *J. Am. Chem. Soc.* 123, 11534–11538 (and the literature cited therein).
- Tsuchiya, T., Kurihara, H., Sato, K., Wakahara, T., Akasaka, T., Shimizu, T., Kamigata, N., Mizorogi, N., Nagase, S., 2006. *Chem. Commun.*, 3585–3587 (and the literature cited therein).
- Weaver, J.H., Chai, Y., Kroll, G.H., Jin, C., Ohno, T.R., Haufler, R.E., Guo, T., Alford, J.M., Conceicao, J., Chibante, L.P.F., Jain, A., Palmer, G., Smalley, R.E., 1992. *Chem. Phys. Lett.* 190, 460.
- Weaver, J.H., Chai, Y., Kroll, G.H., Jin, C., Ohno, T.R., Haufler, R.E., Guo, T., Alford, J.M., Conceicao, J., Chibante, L.P.F., Jain, A., Palmer, G., Smalley, R.E., 1992. *Chem. Phys. Lett.* 190 (5), 460–464.
- Wiener, H., 1947. *J. Am. Chem. Soc.*, 17–20.
- Yannoni, C.S., Hoinkis, M., De Vries, M.S., Bethune, D.S., Salem, J.R., Crowder, M.S., Johnson, R.D., 1992. *Science* 256 (5060), 1191–1192.